Chapter 1

Introduction

1.1 Basic properties of ferroelectrics

All dielectrics can be electrically polarized and they show a dipole moment per unit volume (electrical polarization, P) when an external field is applied. Ferroelectrics are a particular class of crystalline dielectrics with a spontaneous polarization that can be switched by the application of external electric field and that remains after the applied field is removed (known as remanent polarization, P_r). This can be observed by placing the ferroelectric in between two metal electrodes and measuring the ferroelectric hysteresis as shown in Fig. 1.1.

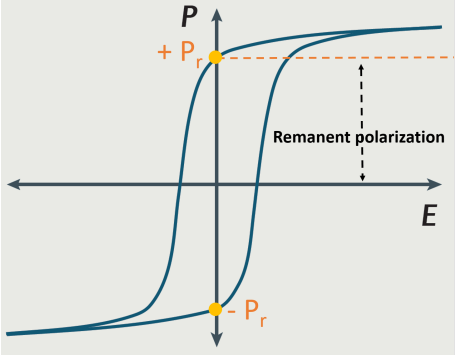

Figure 1.1: *Typical ferroelectric hysteresis loop. [1]*

The macroscopic polarization (P) arises from collective ionic displacements (unit cell dipoles) and, therefore, the ferroelectric nature of a material depends crucially on its crystal symmetry. As shown in Fig. 1.2, among 32 crystal classes, 11 of them are centro-symmetric and cannot host a dipole moment. Among the remaining 21 asymmetric crystal classes, there are 20 showing a polarization change once mechanical stress is applied, that is showing the piezoelectric effect. Moreover, 10 of these 20

classes are intrinsically polar, and display a polarization even in the absence of electric field. If such polarization can be switched by an external electric field, the material is ferroelectric. The polarization remains in the material until up to the Curie temperature (T_c), at which disorder becomes as strong as the dipolar interactions, destroying the macroscopic polarization. Above T_c, the material becomes paraelectric and centrosymmetric. This temperature-dependent behavior, with a strong decrease of P makes ferroelectrics also pyroelectric, that is they can produce a current through an external circuit due to the electron reorganization that takes place upon a change in P, in order to adapt to the new conditions for the screening of the surface polarization charges. However, pyroelectric materials are ferroelectric only if the polarization can be switched. As a consequence, from the viewpoint of the structure, the crystal class of a ferroelectric material must be polar, although not all polar materials are ferroelectric.[2, 3]

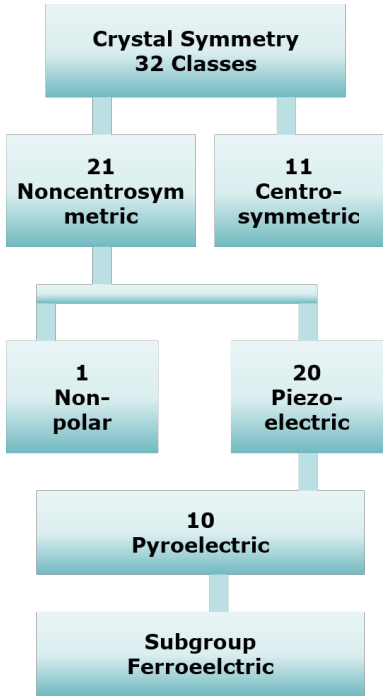

Figure 1.2: *Schematic representation of the piezoelectric, pyroelectric and ferroelectric materials classes on the basis of crystal symmetry. (modified from Ref [4])*

A large class of ferroelectrics are those with the perovskite structure, with chemi-

cal formula ABO_3. The structure of a typical perovskite ferroelectric material $BaTiO_3$ is shown in Fig. 1.3. The structure consists of corner-sharing oxygen octahedra and, for each octahedron, there is a cation B (Ti^{4+}) in the central position and A cations occupy the spaces between the octahedra. Below T_c, the structure is polar, the shift of B cations away from the central position will induce a net dipole moment showing polarization whose direction and magnitude depend on the B cations displacement (and in some materials also on the displacement of A-cations) with respect to the center of charges defined by the oxygen octahedra. With increasing temperature, the cation displacement can change direction and the ferroelectric can go through different phase transitions. In the case of $BaTiO_3$, the structure changes from rhombohedral, at low temperatures, to orthorhombic and to tetragonal, with polarization along [111], [011] and [001] directions, respectively, before it reaches the cubic paraelectric phase (with no cation displacement) at T_c. As shown in Fig. 1.3, these transitions are accompanied by anomalies in the dielectric permittivity, being this the strongest at T_C.

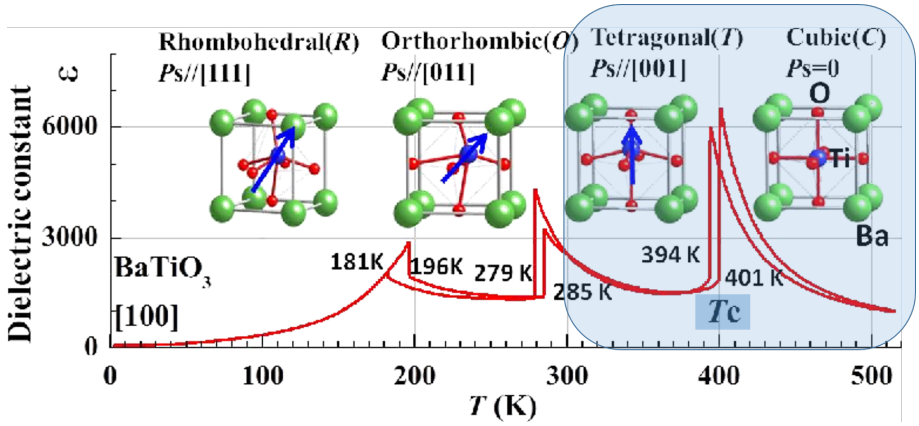

Figure 1.3: *The dielectric permittivity and structures of a $BaTiO_3$ single crystal with increasing temperature (the transition across T_c is marked in blue region). The schematics of Ti displacement in the oxygen octahedron of the perovskite structure are also shown.[5]*

In terms of the microscopic mechanisms of the phase transition, ferroelectrics can be classified in two main types: if the macroscopic polarization disappears above T_c in such a way that the ion displacements that give rise to the polarization vanish locally, this type of transition is called ***displacive***.[6, 7] If the ionic displacements persist into the paraelectric phase but they become random, such that the net polarization vanishes, the ferroelectric transition is of the ***order-disorder*** type. Fig. 1.4,

shows three examples of order-disorder ferroelectrics caused by the $[Me_4N]^+$ cation in $[Me_4N]_2ZnI_4$ and $[Me_4N]CdBr_3$ or the H^+ in hydrogen-bonded $[Hdbco]ReO_4$ being able to displace along several directions, that are symmetric with respect to the high symmetry position. Although the local symmetry-breaking distortions are present in every single unit cell, they are randomly oriented due to the disorder and the short-range order is destroyed, even though with the long-range order, thus the net polarization, is zero.[6, 7]

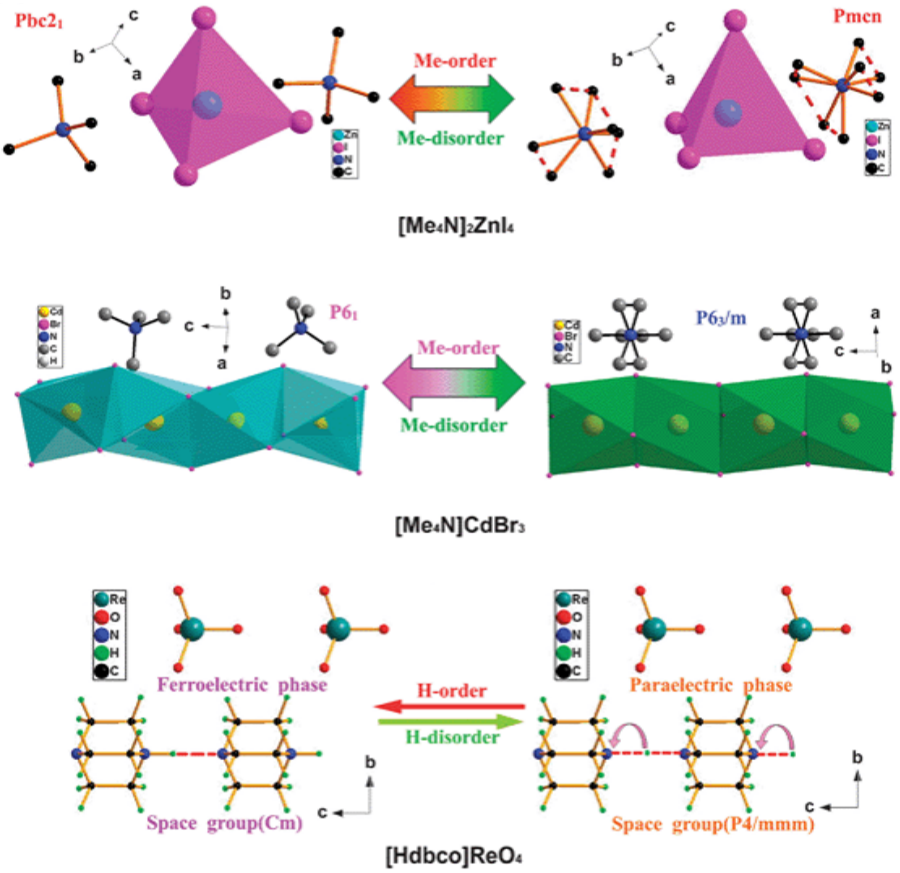

Figure 1.4: *Order–disorder-type ferroelectrics: the order-disorder of the $[Me_4N]^+$ cation in $[Me_4N]_2ZnI_4$ and $[Me_4N]CdBr_3$, and the H^+ ion order–disorder in hydrogen-bonded $[Hdbco]ReO_4$, induce a ferroelectric-paraelelctric transition.[7]*

Besides cation displacements, other more exotic mechanisms for ferroelectricity exist. If the driving force for ferroelectricity only involves electronic charge

displacement, without ionic displacement, the materials are called ***electronic ferroelectrics***. One typical example is charge ordering induced ferroelectricity, such as in $LuFe_2O_4$.[8], where the Fe ions in each layer display an ordered arrangement of valence states of Fe^{2+} and Fe^{3+}, arising from geometrical frustration on a triangle lattice, inducing ferroelectricity. In addition, magnetic frustration can also induce ferroelectricity. In 2003, Kimura et al. found that magnetic ordering in $TbMnO_3$ induces electric polarization[9] showing both magnetic and ferroelectric order, which soon led to the discovery of a dozen of similar materials[10, 11]. However, the polarization induced in this way is typically small ($< 1\mu C/cm^2$) and limited to low temperatures.

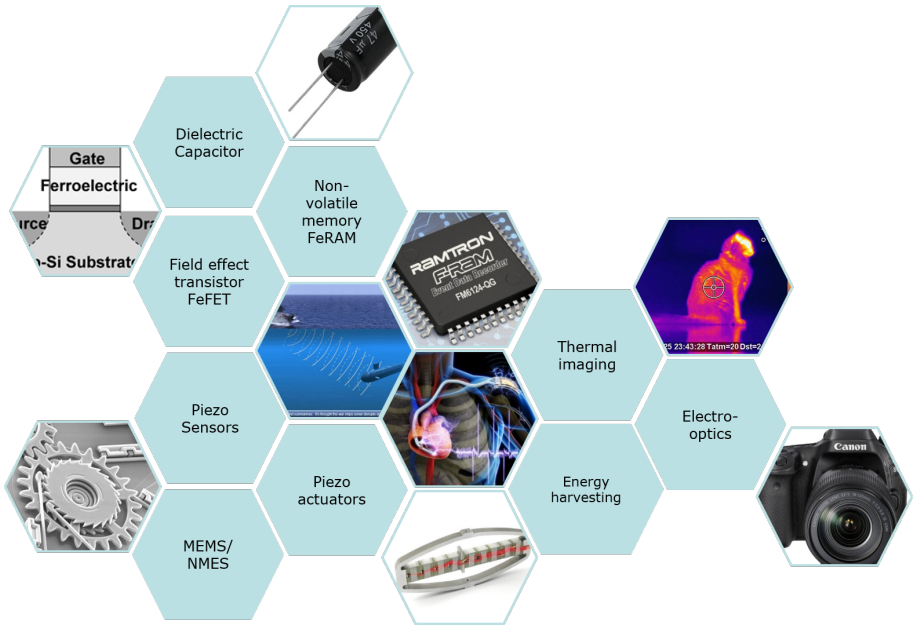

Figure 1.5: *Application of ferroelectrics as piezoelectric, pyroelectric, high-κ dielectric and electro-optical materials. (modified from Ref [4])*

Ferroelectrics are of great interest for many different applications. Many of them do not use the ferroelectricity itself but one of the related properties, since ferroelectrics are also piezoelectric and pyroelectric.[12] Piezoelectrics (which can generate electricity in response to applied mechanical stress) are widely applied in micro/nanoelectromechanical systems[13] (MEMS/NEMS), in particular as actuators or sensors, such as the surface acoustic wave (SAW) sensors that exist in many electronic de-

vices to allow accurate measurements of pressure, strain, temperature or mass. Pyroelectrics (which generate electricity in response to temperature changes) are useful in energy harvesting, thermal imaging (night vision), fire detectors, electro-optics and so on, as shown in Fig. 1.5. Given the existence of switchable spontaneous polarization in ferroelectrics, they can be used in microelectronics as non-volatile Random Access Memory (FeRAM) elements[14] or ferroelectric field effect transistors (FeFETs)[15, 16].

1.2 Issues of conventional ferroelectrics in modern electronic devices

There are different types of commercially available mainstream memories. For example, for high speed processing units (in the ns range), dynamic and static random access memories (DRAM, SRAM), which are volatile, are widely used. For information storage, the low cost, high retention but slow access time (in ms) magnetic hard drive disk dominated the market until the flash memory and solid state drive (SSD) appeared. Considering the fast access time in volatile RAM and the slow access time in non-volatile hard-disk drives, there is a big gap between them, and although flash and SSD have reduced it, there are still strong demands to fill this gap. The ultimate purpose is to combine RAM and high density data storage, requiring fast write and read speed, high endurance and retention, and low energy consumption, which is a huge challenge to realize.[17–19]

With this background, many promising emerging memories show up, such as resistance random access memory (RRAM), magnetoresistive memory (MRAM), phase change memory (PCM), ferroelectric memory (FeRAM, FeFET) which is the main interest in this thesis, and so on. All of them have their specific advantages, and drawbacks that need to be addressed. It is not our purpose to discuss here which memory type is more promising for the future market. In fact, the concept of ferroelectric memory has come up in the last century.[20–22] The two stable remanent polarization states of + P and - P could be used as the 1 and 0 bits (binary digits) used in all modern computers for memory storage and logic operations. Although they have many advantages, eg. low power and non-volatility, and FeRAM has been considered as an established technology since the early 1990s, there are still many issues which limit its market. Some of them, which are considered the most limiting ones by the community, are discussed in the following:

With increasing demand for devices miniaturization to improve information storage, the decreasing size of materials is necessary. In ferromagnets, with decreasing size of the ferromagnetic nanoparticles, the magnetic anisotropy energy decreases.

When the energy is overcome by the thermal fluctuation, the magnetic moments will randomly orient and the material becomes superparamagnetic.[23] In analogy to ferrromagnets, it brings us the term "superparaelectric" in ferroelectrics under size reduction. But the mechanisms are more complicated in ferroelectrics than in ferromagnets. In principle, ferroelectricity can exist only one unit cell, since its energy have been reported sufficient to be resistant to thermal fluctuations. However, in fact, ferroelectricity is also limited by the practical issue of growing high-quality samples with atomic control and, by the electrical boundary conditions. Thus the critical size below which ferroic order disappears is usually much bigger in ferroelectrics.[23, 24] In this case, this type of materials are not suitable for the facile fabrication of 3D capacitors structures which requires a thickness of only a few tens of nanometers.[25] In addition, even if current lithographic techniques allow defining features down to a few nanometers, the crystal structure of complex oxides does not survive the lithographic steps at the borders of the objects, which makes miniaturization of ferroelectric devices very challenging.

As mentioned, one of important factors with respect to **size limitation** is sample quality, which is strongly dependent on the growth techniques. In ferroelectric thin films, dead layers, grain boundaries, and defects such as oxygen vacancies all influence the ferroelectric properties. In addition, the electrostatic boundary conditions play a predominant role, in particular for very thin films. Fig. 1.6(a) depicts a simple electrostatic model.[23, 26] In a thin film of ferroelectric material sandwiched between two ideal metal electrodes, the surface charges induced by the polarization, P, can be completely compensated by the metal. However, with realistic electrodes, the finite screening length leads to incomplete screening of the polarization charges as shown in Fig. 1.6(b), with the corresponding charge distribution, electrical potential and electric field profiles shown in Fig. 1.6(c). Thus, the incomplete screening induces a depolarization field (E_d), expressed as:

$$E_d = -2\frac{\lambda_{eff}}{d\epsilon_0}P \tag{1.1}$$

where λ_{eff} is effective screening length of the system, d is the film thickness and P is polarization of ferroelectric thin film. Accordingly, a smaller λ_{eff}, indicating a better metal, which can better screen the surface charges, the smaller the depolarization field. In real metals λ_{eff} is always finite. In addition, because the E_d arises from the integral of the electrical potential, V, across the film thickness (Fig. 1.6(c)), the depolarization field increases inversely proportional to the thickness, and eventually suppresses ferroelectricity for ultra thin film.[27, 28] In order to avoid this field, the material can create domain walls (domains with opposite orientation of the polarization) or other defects.[29–31]

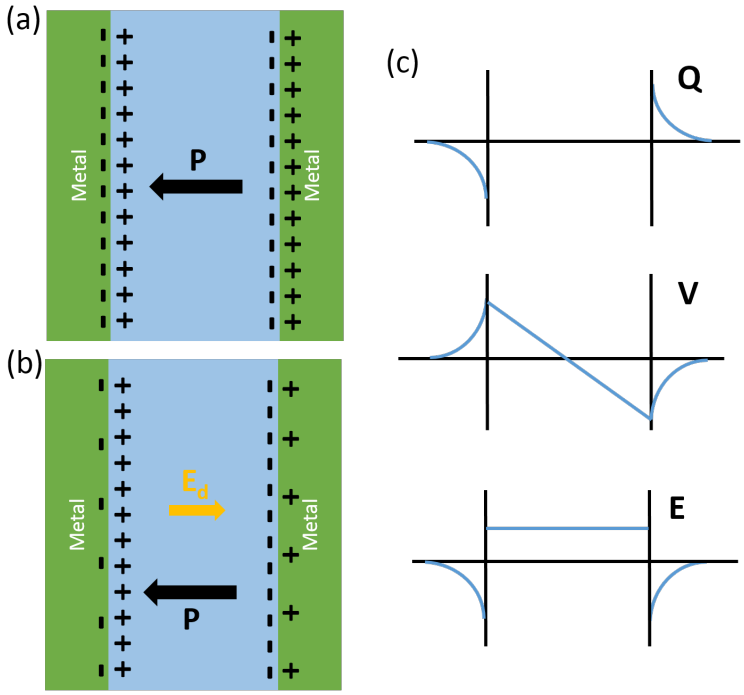

Figure 1.6: *(a) Sketch of a ferroelectric film sandwiched between two ideal metallic electrodes, providing full screening of the polarization charges: there is no depolarization field; (b) the same ferroelectric layer in between two real electrodes, with finite screening length, leading to incomplete screening of the polarization charges and to depolarization field E_d; (c) charge distribution, voltage and electric field profile with realistic electrodes[23, 26] corresponding to (b).*

Another issue is the Silicon compatibility. Nowadays most of the electronic devices in our daily life are built on a chip using Si-based technology, often referred to as CMOS (complementary metal-oxide-semiconductor) technology. Ferroelectric thin films with the largest P and best performances, such as $Pb(Zr,Ti)O_3$ (PZT), $BaTiO_3$ (BTO) or $SrBi_2Ta_2O_9$ (SBT), usually have the perovskite structures, which display **poor CMOS-compatibility**, hampering its widespread application in the industry. Although some epitaxial perovskite films have been developed to grow on a Si substrate[32–34], the interface between the ferroelectric layer and Si substrate is still often far from perfect.[35] Usually, an interfacial SiO_2 dead layer is formed which will influence the quality of the perovskite films, and easily results in the depolar-

ization field causing stability problems of the two polarization states of memory or logic devices.

Last, there are also some **environmental problems**, such as issues related to the lead containing materials (lead zirconate titanate, PZT), known to show the best piezoelectric and ferroelectric properties. Thus, for wider applications of ferroelectrics in people's daily life, environmentally-friendly lead-free materials with comparable excellent properties are urgent to develop as evidenced from the legislation passed by the European Union.[36]

1.3 A new type of ferroelectrics: HfO_2-based thin films

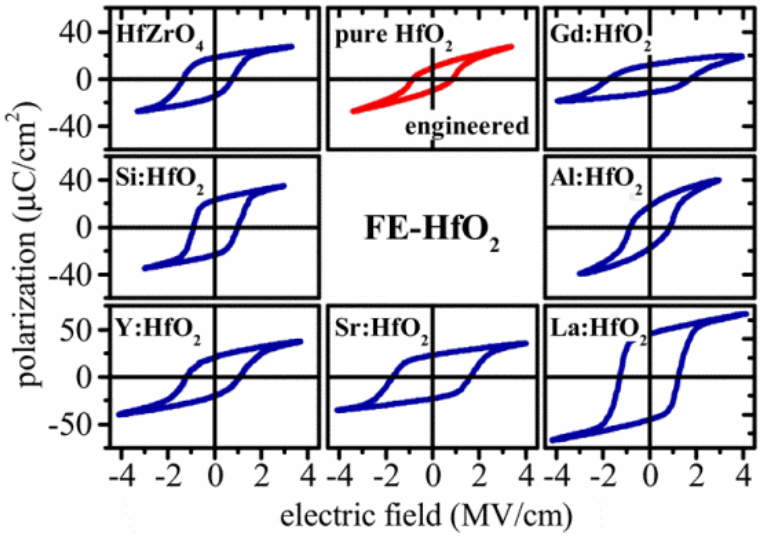

Figure 1.7: *P-E hysteresis loops of HfO_2-based metal-insulator-metal capacitors, revealing ferroelectric properties for different dopants in ultra-thin HfO_2. The polarization is ranging from 10-45 $\mu C/cm^2$. Reprinted from Ref [37].*

Searching for ways to solve the issues discussed in the previous section is a urgent task for the future development of ferroelectric memories and other related devices. Important progress in this direction has been achieved since 2011, when ferroelectricity in Si-doped HfO_2 thin films was firstly reported.[38] Short after,it was shown that various other dopants, such as Zr, Al, Y, Gd, Sr, La and others can also induce ferroelectricity in thin HfO_2 films, as shown in Fig. 1.7. Some of them give rise to very large remanent polarization up to 45 $\mu C/cm^2$, comparable to that

in the best perovskite ferroelectrics. Furthermore, they can be extremely thin (< 10 nm). A remarkable feature is that With increasing thickness, ferroelectricity in Hf-based films disappears, which is at odds with the concepts discussed in the previous section based on the expected trend for the depolarization fields: hafnia-based ferroelectrics only show ferroelectricity at the nanoscale, where other ferroelectrics loose it. In addition, HfO_2 is a simple oxide and it is Si-compatible (in its amorphous form, it has been widely used as the gate insulator in FET manufacturing) and has a large bandgap (> 5 eV), making it less prone to leakage. All of these advantages compared to the conventional perovskite ferroelectrics are believed to overcome the barriers for the application of ferroelectrics in memories, including FeFET and 3D capacitors. Thus, the recent discovery of ferroelectricity in ultrathin layers of HfO_2-based materials represents a real breakthrough in the field.[39, 40]

1.3.1 The origin of ferroelectricity in HfO_2-based films

Very similar to HfO_2 is ZrO_2. The same valance and ionic radius lead to very similar crystal structure and phase diagram. The higher abundance of Zr in comparison to Hf, makes ZrO_2 substitutions highly desirable. Interestingly, the surface energies of both materials differ, and so does their phase stability under size reduction,[41–44] leading to the interesting behaviour of the solid solution.

In bulk, the stable form of HfO_2 (ZrO_2)-based compounds is a monoclinic phase ($P21/c$, m-phase) at room temperature[45, 46]. The high-temperature and high-pressure phases, namely, tetragonal ($P42/nmc$, t-phase) and cubic ($Fm3m$, c-phase) phases[45, 46], can be stabilized at room temperature via doping[47] or nanostructuring[41, 42]. In addition, rhombohedral phases (r-phase) have also been obtained by doping and applying mechanical stress[48–50]. The t- and r-phases are distortions from the fluorite structure (c-phase) and have a significantly lower volume than the m-phase. None of the above-mentioned phases is reported to be polar.

Recently, several theoretical works have modelled the possible phases that could give rise to ferroelectricty in this new type of materials.[51–53] There is a polar orthorhombic phase (space group $Pca2_1$, o-phase) which is consistent with the experiment. This phase was first reported for Mg-doped ZrO_2 ceramics when cooled to cryogenic temperatures[54] and calculations find this phase as the most plausible polar distortion of the tetragonal fluorite phase (relatively close in energy). Thus this polar phase is believed to be the structural origin for the recently reported ferroelectricity in HfO_2-based thin films[39]. Recent literature has gathered examples of hafnia-based ferroelectric films with different dopants[55–57], on different substrates Si[39] and Y-ZrO_2[58], with different electrodes (that is, TiN[59], Pt[60], Ir[61], TaN[62] and Si[63]) and by different growth methods (atomic layer deposition (ALD)[64], chemical solution deposition[65], pulsed laser deposition (PLD)[58] and

chemical vapour deposition[66]). Various possible mechanisms, such as stress[67, 68], doping[62], confinement by the top electrode[59] or surface energy[69–71], were put forward as stabilizing factors for the ferroelectric phase.

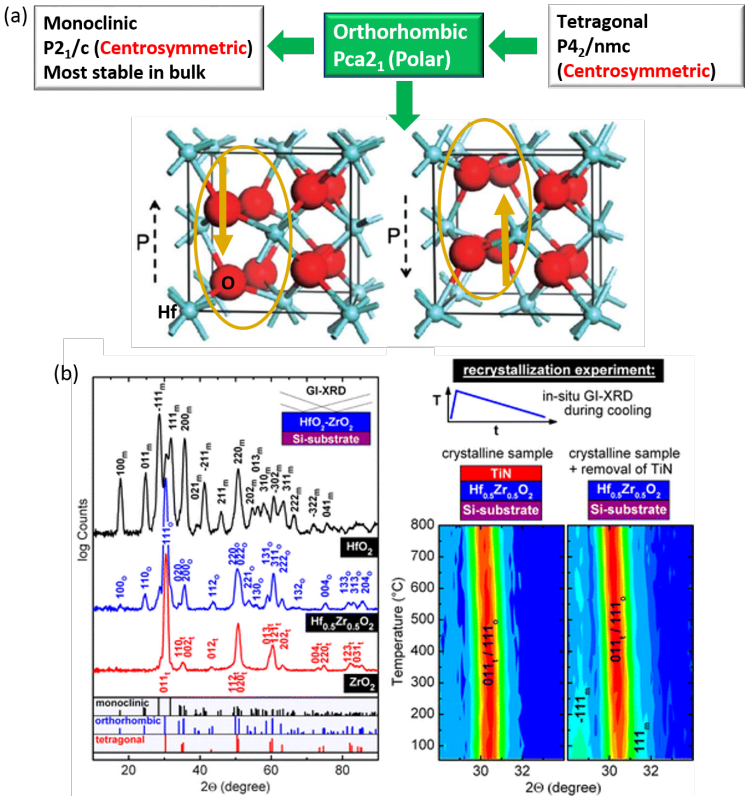

Figure 1.8: *(a) Current understanding of the origin of ferroelectricity in HfO2-based ferroelectrics. Structure picture is modified from Ref [38]; (b) GI-XRD diffractograms of 9 nm ZrO_2, $Hf_{0.5}Zr_{0.5}O_2$, and HfO_2 thin films (left); In situ GI-XRD measurements during cooling (right). Reprinted from Ref [71].*

As shown in Fig. 1.8(a), the polar o-phase has been postulated as the transformation phase between the t- and m-phases.[54, 62, 72]. Due to the larger surface energy of ZrO_2 compared to HfO_2, for a given particle size of 9 nm, at room temperature, undoped HfO_2 is in its monoclinic ground state, while ZrO_2 is transformed to the low volume tetragonal phase, as shown in Fig. 1.8(b) and reported in ref[71]. According to this, a phase transition between the monoclinic and the tetragonal phases

should take place at intermediate compositions of the $Hf_{1-x}Zr_xO_2$ solid solution. This transition happens through an intermediate bridging phase (with a molecular volume in between that of the tetragonal and the monoclinic phases), which is the polar (ferroelectric) orthorhombic phase that can also be stabilized in doped HfO_2, as described previously. In particular, in the case reported in ref.[71], for the given particle size in 9 nm film, the ferroelectric phase takes place at a $Hf_{0.5}Zr_{0.5}O_2$ composition. In short, all the routes described above (doping, confinement and nanostructuring) have the effect of increasing the molar volume with respect of that of the fluorite phase, stabilizing the intermediate ferroelectric phase. An exhaustive overview of these findings can be found in the recent monograph "Ferroelectricity in doped Hafnium oxide: materials, properties and devices".[40]

No matter what the route to ferroelectricity is (doping or confinement, the size of the ferroelectric domains are always around 10 nm. Initially, the best ferroelectric properties were reported only in ultrathin films (usually around 10 nm thick)[64, 73, 74]. The polarization declined significantly with increasing thickness as a result of the appearence of the nonpolar m-phase[74]. More recently, ferroelectricity has been found in thicker films (50 to 390 nm)[65, 75], but in these the average grain size is still around 10-20 nm. Thus, all reported ferroelectric hafnia-based films have in common that they are formed by small crystallites, emphasizing the crucial role played by size effects in stabilizing the ferroelectric phase[71]. Indeed, it is known that in nanoparticles of radius r, the surface energy (σ) can produce large internal pressures ($P = 2\sigma/r$) of the order of a few GPa[76, 77]. Thus, small crystals will prefer the room-temperature stability of lower-volume c- or t- phases rather than the m-phase[78–80]. For thicker films, usually above 10 nm (where the crystals have the possibility to grow further), the m-phase (bulk) is always present.[40]

Most works report on ALD-grown films, which are polycrystalline and contain multiple phases (m-, t- and o-phases) as shown in Fig. 1.8(b). In addition, the similarity of these structures and the small size of crystallites make a complete structural characterization even more challenging. Therefore, well-oriented or epitaxial samples, preferably in a single phase, are desired to study the factors contributing to ferroelectricity. By the PLD method, single-crystal, epitaxial Y-doped HfO_2 films have been achieved on yttrium oxide-stabilized zirconium oxide substrates with the polar o-phase[58], reaching a polarization of 16 $\mu C/cm^2$. In this thesis, we also ultilize the PLD method to grow epitaxial films on different substrates,[81], which has enabled more insights into the origin of ferroelectrcity in this type of materials (see *Chapter 3*).

1.3.2 Perspectives of ferroelectric HfO_2-based films in applications

Since 2011, when ferroelectricity was found in Si-doped HfO_2, this material has already attracted many interest from the scientific community. There are several device geometries for which ferroelectric HfO_2-based films could represent huge progress. Some of them are listed here:

- **Ferroelectric memory**

Because of the various advantages mentioned above, such as nanoscale ferroelectricity, CMOS compatibility, HfO_2-based ferroelectrics are very promising to be applied as memories[39, 82] using its bi-stable polarization, and a few works has been reported towards this direction, using hafnia-based ferroelectrics as random-access memories (FeRAM),[83] or field-effect transistors (FeFET),[84, 85].

FeRAM was regarded as a promising candidate for the next generation of non-volatile memories and many works has been reported in this direction,[14, 22], but FeRAMs have not achieved wide commercial use. One of the disadvantages is that the read process is destructive and rewrite is needed after every reading pulse.[86] Thus nondestructive read architectures, which are based on measuring resistance states upon changes of polarization rather than detecting capacitance changes, are strongly preferred.[87] For example, in FeFET with the gate oxide being a ferroelectric material, the readout can be nondestructive, with the polarization direction of the gate changing the magnitude of source-drain channel current.[16] In addition, based on these two concepts (FeRAM, FeFET), ferroelectric tunnel junctions have also emerged.[88–91] They are two-terminal devices, similar in geometry to the capacitor stack in FeRAMs, but (as in FeFET) the measured resistance depends on the polarization direction of the ferroelectric barrier: the change in the electronic barrier height or barrier width that take place due to the surface charges generated at the interface with the metal electrodes,[92] results in modifications of the tunnel currents. This will be further discussed in the following section.

- **Tunnel junctions**

To miniaturize the ferroelectric memory devices to the size of a few nanometers, ferroelectric tunnel junctions (FTJ) have brought lots of interest. The polarization direction could control the tunnel current across the ferroelectric barrier on and off. The challenge is to keep the tunnel barrier ferroelectric and defect-free down to the 4-5 nm needed for tunneling. The advantages of nanoscale ferroelectricity and large bandgap of HfO_2-based materials compared to conventional perovskite ferroelectrics, [93–97], make it ideal to be integrated into FTJ devices. In addition, if

the electrodes are magnetic, multiferroic tunnel junctions (MFTJs) can be developed, enabling multifunctional device application. The working principles are explained below:

Ferroelectric tunnel junction is a tunnel junction in which two metal electrodes are separated by a thin ferroelectric layer as shown in Fig. 1.10(b). The polarization of the FE layer can be switched by the external electric filed, which results in an electric resistance change between (R_{high} and R_{low}). This phenomenon is known as tunneling electroresistance (TER). Its origin has been mainly ascribed to three possible mechanisms as shown in Fig. 1.9[88]: a) incomplete charge screening at ferroelectric/electrode interfaces affecting the potential barrier profile; b) the change in the position of ions at the interfaces after polarization reversal, or/and c) the strain difference induced by the electric field in the ferroelectric barrier.

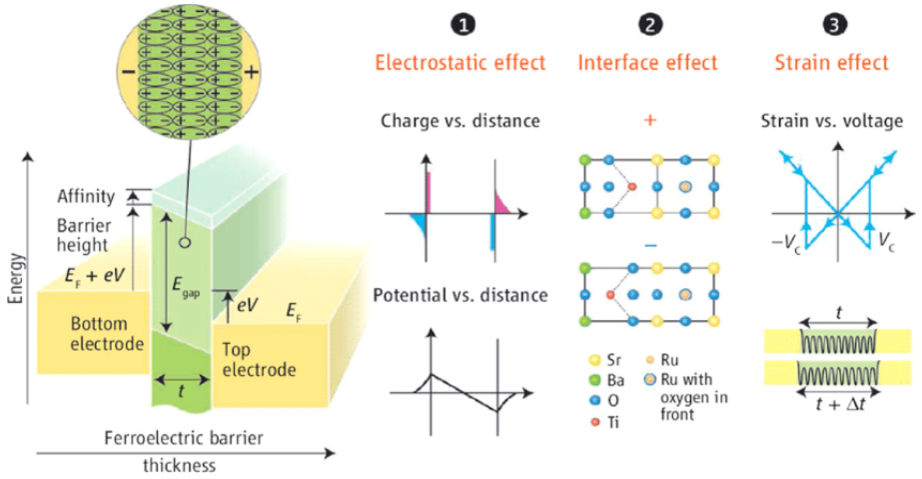

Figure 1.9: *A ferroelectric tunnel junction. The possible mechanisms that induce electroresistance are illustrated. Reprinted from Ref [88].*

A magnetic tunnel junction (MTJ) consists of two layers of magnetic metal separated by an ultrathin layer of insulator, as show in Fig. 1.10(a). Due to such thin insulating layer, when a bias voltage is applied between two electrodes, electrons can tunnel through the barrier. And this tunneling current is dependent on the relative orientation of magnetizations of the two ferromagnetic layers, which can be manipulated the external magnetic field. Usually, when they are aligned in parallel, the junction shows low resistance, while in antiparallel configuration, it shows high resistance. This phenomenon is well known as tunneling magnetoresistance (TMR),

which is a consequence of spin-dependent tunneling.

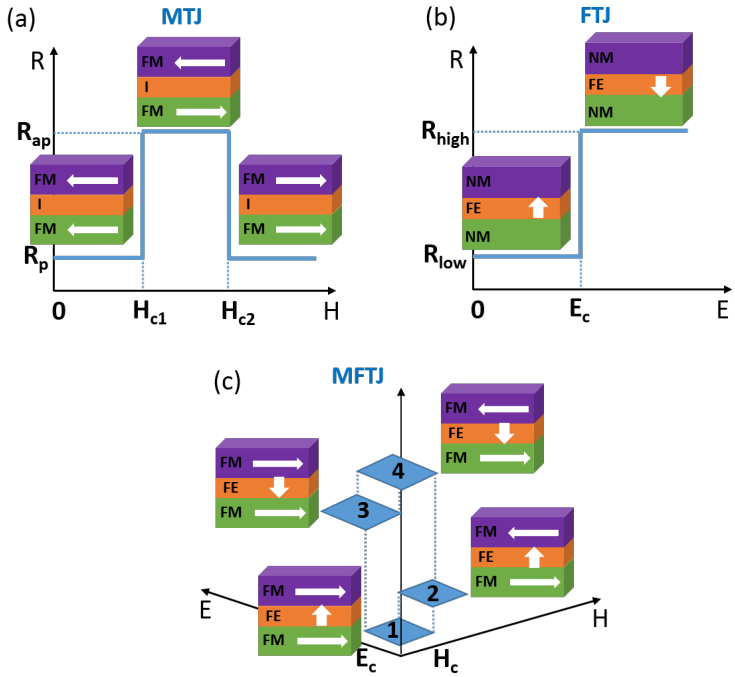

Figure 1.10: *Schematic drawing of resistive switching in (a) magnetic tunnel junction (MTJ), (b) ferroelectric tunnel junction (FTJ), and (c) multiferroic tunnel junction (MFTJ). Reproduced from Ref [98].*

According to the simple model by Julliere [99], the electron spin is assumed to be preserved during tunneling, and the tunnel current of each spin species is proportional to the product of the Fermi level density of state (DOS) of the two electrodes. As a result, for two ferromagnetic (FM) metals with different DOS at the Fermi level, the total tunnel current of spin-up and spin-down electrons will depend on the relative magnetic configuration of these two FM layers, as shown in Fig. 1.11. Hence, TMR effect depends on the DOS asymmetry of the FM for the two spin channels.

TMR can be understood in terms of Julliere's model as [99],

$$\frac{\Delta R}{R} = \frac{(R_{AP} - R_P)}{R_P} = \frac{2P_1P_2}{(1 - P_1P_2)} \tag{1.2}$$

where R_{AP}:antiparallel resistance; R_P: parallel resistance; P_1, P_2: spin polarization of two FM layers.

The magnitude of TMR is determined by the spin polarization P of the DOS at the Fermi energy of the two ferromagnetic layers, P_1 and P_2 correspondingly.

$$P = \frac{(n_\uparrow(E_F) - n_\downarrow(E_F))}{(n_\uparrow(E_F) + n_\downarrow(E_F))} \tag{1.3}$$

1

where $n_\uparrow(E_F)$: number of electrons with upward spin polarization; $n_\downarrow(E_F)$: number of electrons with downward spin polarization.

Based on TMR effect, MTJs have been widely used as the read-heads of modern hard disk drives[100], and magnetoresistive random-access memory (MRAM) [101].

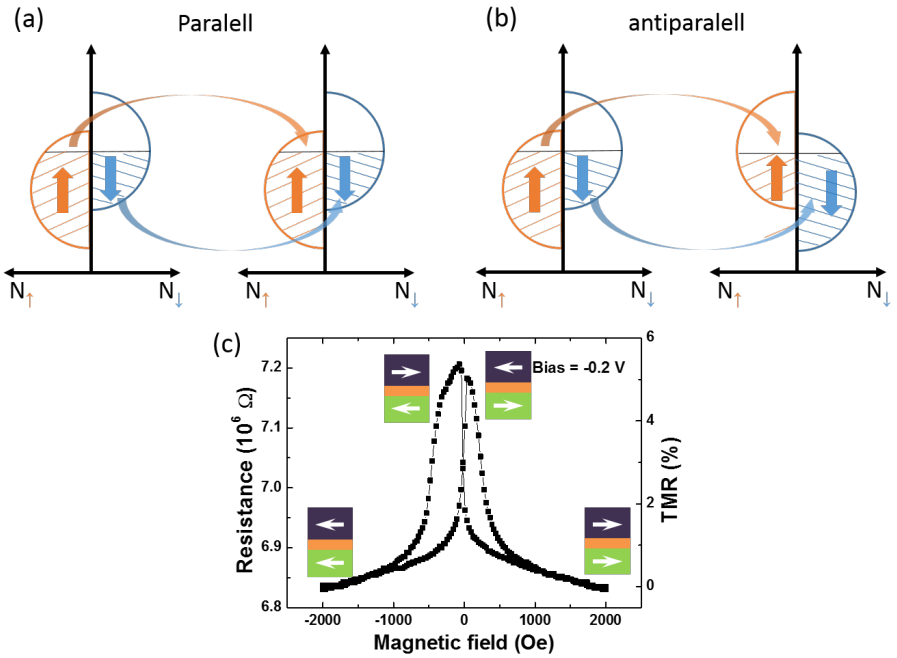

Figure 1.11: *Schematic drawing of the TMR effect for parallel (a) and antiparallel (b) configurations. (c) A typical magnetoresistance curve of an MTJ junction with LSMO/HZO/Co structure. (Data from Ref [102])*

Multiferroic tunnel junctions employ a ferroelectric tunneling barrier between two ferromagnetic electrodes. Given both ferroic orders, the TMR (of MTJs) and TER (of FTJs) effects can be combined in one system, which produces four resistance states by magnetic field and electric field switching, as shown in Fig. 1.10(c). Moreover, the interplay among magnetic, electric, and transport properties in this artificial

multiferroic heterostructures, brings much interest due to its various combinations for device design and stronger magnetoelectric coupling (ME) compared to single phase/crystal multiferroics.[103–106] The ME coupling in MFTJs can be quantified by the tunneling electromagnetoresistance (TEMR) effect[107], which can be defined as:

$$TEMR = \frac{(TMR_{V+} - TMR_{V-})}{TMR_{V-}} \tag{1.4}$$

where V+: positive electric pulse; V-: negative electric pulse.

MFTJs have already drawn considerate attention, driven by its potential application in multilevel memories and electric-field controlled spintronics, promoting low-power and fast-speed devices.[105, 106, 108, 109] This is the type of devices that are studied in this thesis (see *Chapters 5 and 6*).

• **Negative capacitance**

In metal-oxide-semiconductor field-effect transistor (MOSFETs), the subthreshold swing (S_{s-th}) indicates how much voltage is needed to change the drain current by one order of magnitude. To improve the energy efficiency of electronics devices, smaller S_{s-th} is expected. According to:

$$S_{s-th} = ln(10)\frac{\kappa T}{q}(1 + \frac{C_d}{C_{ox}}) \tag{1.5}$$

where C_d is the depletion layer capacitance; C_{ox} is the gate-oxide capacitance and $\frac{\kappa T}{q}$ is the thermal voltage. The minimum S_{s-th} is limited by $ln(10)\kappa T/q$ due to the Boltzmann distribution of electrons.[110–114] Thus the concept of negative capacitance provides a solution to push S_{s-th} beyond the existing limitation (60 mv/dec) and can promote the super low-power transistors.

It has been shown that ferroelectrics can have negative capacitance. [110, 115, 116] The origin of the negative capacitance in ferroelectrics is the negative slope region of the energy barrier in a double-well potential landscape.[117] Recently, Hoffmann et al. showed that it is possible to stabilize the negative capacitance state with ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ thin films integrated into a heterostructure capacitor with a second dielectric layer to slow down the screening of polarization charges during switching. That is, they could access the unstable S-shape part of the ferroelectric hysteresis loop that corresponds to the transient negative slope region of the ferroelectric Landau potential.[116] Several other works have also reported the advantages and feasibility of negative capacitance with ferroelectric doped-HfO_2.[118–120]

• **Energy harvesting**

As all ferroelectrics, doped-HfO_2 materials are also piezoelectric and pyroelectric and, thus, suitable to transform mechanical or thermal energy into electricity. Ferroelectrics can generate relatively large potential differences (scaling with their thickness) when connected to an external circuit, but due to their good insulating properties, they offer very low currents (scaling with their surface area), resulting in low power outputs of tens of microwatts to, possibly, miliwatts for highly optimized materials. These low values, compared to other ways of energy harvesting, such as photovoltaics, have dismissed ferroelectrics as good candidates for energy harvesting. However, this perception is recently changing, as low power generation has nowadays a huge potential due to the need for autonomously powering of sensors (most sensors consume milliwatts or lower power) for the internet of things (IoT), self-driving cars, smart cities, etc. In addition, microelectronic devices become smaller and require increasingly lower power (i.e. nowadays it is possible to find microprocessors that consume as little as microwatts) and it is not unexpected that the power required for personal electronics will reach the milliwatt level in the not so far future. Thus, research into ferroelectrics for energy harvesting should be encouraged. For such a future, currently optimized lead-containing materials are not suitable and research on highly sustainable ferroelectrics made of simple oxides and abundant elements is needed.[121] Thus the recently reported ferroelectric doped-HfO_2 film is a very good candidate.[65, 122–124]

• **Synaptic devices**

In recent years, artificial intelligence has brought significant breakthroughs in our daily life[125] However, this is still based on complex algorithms and the handling of large amounts of data and requires the use of supercomputers, which is very energy-consuming. One way to alleviate that is to think of different computer architectures and different ways of computing that can deal with big data in a more efficient manner. For that, inspiration is taken from the human brain, which receives large amounts of sensory data and can classify data, prioritize information and recognize complex patterns using a fraction of the power that a supercomputer does to perform a similar task. For that, the plasticity of the neurons and synapses in the brain need to be emulated. Thus new brain-inspired materials need to be urgently developed.[126] These materials are refereed to as memristors. Memristor behavior, which shows adaptable conductance, is very promising for synaptic devices. Ferroelectric materials can show memristive behaviour, since their resistance in a capacitor configuration varies with the volume fraction of the switched polarization under the electrode, thus the polarization domain dynamics by different voltages pulses

can be used to create artificial synapses.[127–129]

1.4 Thesis outline

The work presented in this thesis aims at understanding the origin of ferroelectricity in this new type of ferroelectric based on HfO_2 ultra-thin films. For that, we focus on the epitaxial growth of these films in order to achieve single phase ferroelectric materials and to improve the quality of the interfaces. The role played by different substrates on the stabilization of the ferroelectric phase is then studied. A specific chemical composition $Hf_{0.5}Zr_{0.5}O_2$ is chosen in most of this work because of its robust ferroelectric behavior, as reported by others, and its larger Zr content (more abundant element than Hf). Furthermore, taking advantage of the unique properties of this material, we integrate it as a tunnel barrier with magnetic electrodes. In this way, the first multiferroic tunnel junctions with ferroelectric HfO_2-based barriers are produced and characterized in this thesis work. This thesis is structured as follows:

Chapter 2: introduces experimental techniques that are used in this work.

Chapter 3: Compared to the usually reported polycrystalline films, we take advantage of high kinetic energy of pulsed laser deposition (PLD) to grow "cleaner" epitaxial films with single phase on $SrTiO_3$ substrates. A novel ferroelectric rhombohedral phase, different from the usually reported polar o-phase, is found in our work. With this phase, a large remanent polarization up to 34 $\mu C/cm^2$ is obtained in ultrathin film down to 5 nm. In addition, we solved an inconvenient technical problem: the wake-up effect. According to the results of our work, we propose a model for the stabilization of this ferroelectric phase, which, as a result, also provides a method to possibly realize nanoscale ferroelectricity in other binary simple oxides.

Chapter 4: $Hf_{0.5}Zr_{0.5}O_2$ thin films are grown on different substrates, mainly on perovskite substrates with different lattice parameters for studying the strain effect, but also on hexagonal substrates with very different chemistry as Al_2O_3 (sapphire). The relationship between the film orientation and phases are investigated. This work provides a rationale to understand the stabilization of the different ferroelectric phases.

Chapter 5: We report for the first time on multiferroic tunnel junction with $Hf_{0.5}Zr_{0.5}O_2$, using an ultrathin ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ barrier of only 2 nm in thickness. The importance of this is that we are able to make actual wire-bonded devices with an

exceptionally large yield. We demonstrate a four resistance states memory due to the combination of TMR and TER effect by magnetic and electric field switching. This will be added to the family of phenomena in which Hafnia-based ferroelectrics are showing to surpass the best classical materials, such as $BaTiO_3$ or PZT.

Chapter 6: Following the work of chapter 5, with electric pulse cycling, a strong magnetoelectric coupling and huge TER are developed in the tunnel junctions. The mechanism of reversed spin-polarization and, concomitantly, massively increased TER are studied in this chapter. We find these effect could be independent from the ferroelectric polarization switching. This work promotes better understanding of this multiferroic system and paves the way for the future possible applications.

Bibliography

[1] L. W. Martin and A. M. Rappe, "Thin-film ferroelectric materials and their applications," *Nature Reviews Materials* **2**(2), p. 16087, 2017.

[2] M. E. Lines and A. M. Glass, *Principles and applications of ferroelectrics and related materials*, Oxford university press, 2001.

[3] F. Jona and G. Shirane, *Ferroelectric Crystals, International Series of Monographs on Solid State Physics*, Pergamon press, 1962.

[4] J. Varghese, R. W. Whatmore, and J. D. Holmes, "Ferroelectric nanoparticles, wires and tubes: synthesis, characterisation and applications," *Journal of Materials Chemistry C* **1**(15), pp. 2618–2638, 2013.

[5] D. Fu and M. Itoh, *Ferroelectric Materials—Synthesis and Characterization*, IntechOpen, 2015.

[6] P. Chandra and P. B. Littlewood, *Physics of ferroelectrics: A Landau primer for ferroelectrics*, Springer, 2007.

[7] T. Hang, W. Zhang, H.-Y. Ye, and R.-G. Xiong, "Metal-organic complex ferroelectrics," *Chemical Society Reviews* **40**(7), pp. 3577–3598, 2011.

[8] N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, *et al.*, "Ferroelectricity from iron valence ordering in the charge-frustrated system lufe2o4," *Nature* **436**(7054), p. 1136, 2005.

[9] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T.-h. Arima, and Y. Tokura, "Magnetic control of ferroelectric polarization," *Nature* **426**(6962), p. 55, 2003.

[10] S.-W. Cheong and M. Mostovoy, "Multiferroics: a magnetic twist for ferroelectricity," *Nature Materials* **6**(1), p. 13, 2007.

[11] N. Hur, S. Park, P. Sharma, J. Ahn, S. Guha, and S. Cheong, "Electric polarization reversal and memory in a multiferroic material induced by magnetic fields," *Nature* **429**(6990), p. 392, 2004.

[12] P. Muralt, "Ferroelectric thin films for micro-sensors and actuators: a review," *Journal of Micromechanics and Microengineering* **10**(2), p. 136, 2000.

[13] C.-B. Eom and S. Trolier-McKinstry, "Thin-film piezoelectric mems," *MRS Bulletin* **37**(11), pp. 1007–1017, 2012.

[14] J. Scott, "Applications of modern ferroelectrics," *Science* **315**(5814), pp. 954–959, 2007.

[15] M. Dawber, K. Rabe, and J. Scott, "Physics of thin-film ferroelectric oxides," *Reviews of Modern Physics* **77**(4), p. 1083, 2005.

[16] S. Mathews, R. Ramesh, T. Venkatesan, and J. Benedetto, "Ferroelectric field effect transistor based on epitaxial perovskite heterostructures," *Science* **276**(5310), pp. 238–240, 1997.

[17] T. Schenk, M. Pešić, S. Slesazeck, U. Schroeder, and T. Mikolajick, "Memory technology – a primer for material scientists." unpublished.

[18] J. Åkerman, "Toward a universal memory," *Science* **308**(5721), pp. 508–510, 2005.

[19] T. Schenk, M. Hoffmann, C. Richter, M. Pesic, S. Mueller, S. Slesazeck, U. Schroeder, T. Mikolajick, D. Pohl, J. Mueller, P. Polakowski, R. Materlik, A. Kersch, X. Sang, E. D. Grimley, and J. M. LeBeau, "Doped hafnium oxide for ferroelectric memories (invited)," in *Materials Research Society Fall Meeting, Boston*, 2015.

[20] J. F. Scott, *Ferroelectric memories*, vol. 3, Springer Science & Business Media, 2013.

[21] J. F. Scott and C. A. P. De Araujo, "Ferroelectric memories," *Science* **246**(4936), pp. 1400–1405, 1989.

[22] O. Auciello, J. F. Scott, R. Ramesh, *et al.*, "The physics of ferroelectric memories," *Physics Today* **51**(7), pp. 22–27, 1998.

[23] C. Lichtensteiger, M. Dawber, and J.-M. Triscone, *Physics of ferroelectrics: Ferroelectric size effects*, Springer, 2007.

[24] P. Ghosez and J. Junquera, "First-principles modeling of ferroelectric oxide nanostructures." preprint on webpage at arXiv preprint cond-mat/0605299, 2006.

[25] D. S. Jeong, R. Thomas, R. Katiyar, J. Scott, H. Kohlstedt, A. Petraru, and C. S. Hwang, "Emerging memories: resistive switching mechanisms and current status," *Reports on Progress in Physics* **75**(7), p. 076502, 2012.

[26] M. Dawber, P. Chandra, P. Littlewood, and J. Scott, "Depolarization corrections to the coercive field in thin-film ferroelectrics," *Journal of Physics: Condensed Matter* **15**(24), p. L393, 2003.

[27] I. Batra, P. Wurfel, and B. Silverman, "Phase transition, stability, and depolarization field in ferroelectric thin films," *Physical Review B* **8**(7), p. 3257, 1973.

[28] P. Wurfel and I. Batra, "Depolarization-field-induced instability in thin ferroelectric films—experiment and theory," *Physical Review B* **8**(11), p. 5126, 1973.

[29] C. Kittel, P. McEuen, and P. McEuen, *Introduction to solid state physics*, vol. 8, Wiley New York, 1976.

[30] S. t. Streiffer, J. Eastman, D. Fong, C. Thompson, A. Munkholm, M. R. Murty, O. Auciello, G. Bai, and G. Stephenson, "Observation of nanoscale 180^{circ} stripe domains in ferroelectric pbtio3 thin films," *Physical Review Letters* **89**(6), p. 067601, 2002.

[31] D. D. Fong, G. B. Stephenson, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, and C. Thompson, "Ferroelectricity in ultrathin perovskite films," *Science* **304**(5677), pp. 1650–1653, 2004.

[32] C. Dubourdieu, J. Bruley, T. M. Arruda, A. Posadas, J. Jordan-Sweet, M. M. Frank, E. Cartier, D. J. Frank, S. V. Kalinin, A. A. Demkov, *et al.*, "Switching of ferroelectric polarization in epitaxial batio3 films on silicon without a conducting bottom electrode," *Nature Nanotechnology* **8**(10), p. 748, 2013.

[33] A. Borowiak, G. Niu, V. Pillard, G. Agnus, P. Lecoeur, D. Albertini, N. Baboux, B. Gautier, and B. Vilquin, "Pulsed laser deposition of epitaxial ferroelectric pb (zr, ti) o3 films on silicon substrates," *Thin Solid Films* **520**(14), pp. 4604–4607, 2012.

[34] J. W. Reiner, A. M. Kolpak, Y. Segal, K. F. Garrity, S. Ismail-Beigi, C. H. Ahn, and F. J. Walker, "Crystalline oxides on silicon," *Advanced Materials* **22**(26-27), pp. 2919–2938, 2010.

[35] M. Takahashi and S. Sakai, "Self-aligned-gate metal/ferroelectric/insulator/semiconductor field-effect transistors with long memory retention," *Japanese Journal of Applied Physics* **44**(6L), p. L800, 2005.

[36] P. Panda, "environmental friendly lead-free piezoelectric materials," *Journal of materials science* **44**(19), pp. 5049–5062, 2009.

[37] J. Müller, P. Polakowski, S. Riedel, S. Mueller, E. Yurchuk, and T. Mikolajick, "Ferroelectric hafnium oxide a game changer to fram?," in *2014 14th Annual Non-Volatile Memory Technology Symposium (NVMTS)*, pp. 1–7, IEEE, 2014.

[38] T. Böscke, J. Müller, D. Bräuhaus, U. Schröder, and U. Böttger, "Ferroelectricity in hafnium oxide thin films," *Applied Physics Letters* **99**(10), p. 102903, 2011.

[39] M. H. Park, Y. H. Lee, H. J. Kim, Y. J. Kim, T. Moon, K. D. Kim, J. Mueller, A. Kersch, U. Schroeder, T. Mikolajick, *et al.*, "Ferroelectricity and antiferroelectricity of doped thin hfo2-based films," *Advanced Materials* **27**(11), pp. 1811–1831, 2015.

[40] U. Schroeder, C. S. Hwang, and H. Funakubo, *Ferroelectricity in doped hafnium oxide: materials, properties and devices*, Woodhead Publishing, 2019.

[41] M. Shandalov and P. C. McIntyre, "Size-dependent polymorphism in hfo2 nanotubes and nanoscale thin films," *Journal of Applied Physics* **106**(8), p. 084322, 2009.

[42] S. Tsunekawa, S. Ito, Y. Kawazoe, and J.-T. Wang, "Critical size of the phase transition from cubic to tetragonal in pure zirconia nanoparticles," *Nano Letters* **3**(7), pp. 871–875, 2003.

[43] W. Zhou, S. V. Ushakov, T. Wang, J. G. Ekerdt, A. A. Demkov, and A. Navrotsky, "Hafnia: Energetics of thin films and nanoparticles," *Journal of Applied Physics* **107**(12), p. 123514, 2010.

[44] M. W. Pitcher, S. V. Ushakov, A. Navrotsky, B. F. Woodfield, G. Li, J. Boerio-Goates, and B. M. Tissue, "Energy crossovers in nanocrystalline zirconia," *Journal of the American Ceramic Society* **88**(1), pp. 160–167, 2005.

[45] O. Ohtaka, H. Fukui, T. Kunisada, T. Fujisawa, K. Funakoshi, W. Utsumi, T. Irifune, K. Kuroda, and T. Kikegawa, "Phase relations and volume changes of hafnia under high pressure and high temperature," *Journal of the American Ceramic Society* **84**(6), pp. 1369–1373, 2001.

[46] O. Ohtaka, H. Fukui, T. Kunisada, T. Fujisawa, K. Funakoshi, W. Utsumi, T. Irifune, K. Kuroda, and T. Kikegawa, "Phase relations and equations of state of zro2 under high temperature and high pressure," *Physical Review B* **63**(17), p. 174108, 2001.

[47] C.-K. Lee, E. Cho, H.-S. Lee, C. S. Hwang, and S. Han, "First-principles study on doping and phase stability of hfo2," *Physical Review B* **78**(1), p. 012102, 2008.

[48] H. Hasegawa, "Rhombohedral phase produced in abraded surfaces of partially stabilized zirconia (psz)," *Journal of Materials Science Letters* **2**(3), pp. 91–93, 1983.

[49] H. Hasegawa, T. Hioki, and O. Kamigaito, "Cubic-to-rhombohedral phase transformation in zirconia by ion implantation," *Journal of Materials Science Letters* **4**(9), pp. 1092–1094, 1985.

[50] D. Burke and W. Rainforth, "Intermediate rhombohedral (r-zro2) phase formation at the surface of sintered y-tzp's," *Journal of Materials Science Letters* **16**(11), pp. 883–885, 1997.

[51] R. Materlik, C. Künneth, and A. Kersch, "The origin of ferroelectricity in hf1-xzrxo2: A computational investigation and a surface energy model," *Journal of Applied Physics* **117**(13), p. 134109, 2015.

[52] M. Dogan, N. Gong, T.-P. Ma, and S. Ismail-Beigi, "Causes of ferroelectricity in hfo2-based thin films: An ab initio perspective," *Physical Chemistry Chemical Physics* **21**, 2019.

[53] S. Barabash, "Prediction of new metastable hfo2 phases: toward understanding ferro- and antiferroelectric films," *Journal of Computational Electronics* **16**(4), pp. 1227–1235, 2017.

[54] E. H. Kisi, C. J. Howard, and R. J. Hill, "Crystal structure of orthorhombic zirconia in partially stabilized zirconia," *Journal of the American Ceramic Society* **72**(9), pp. 1757–1760, 1989.

[55] J. Müller, T. Böscke, S. Müller, E. Yurchuk, P. Polakowski, J. Paul, D. Martin, T. Schenk, K. Khullar, A. Kersch, *et al.*, "Ferroelectric hafnium oxide: A cmos-compatible and highly scalable approach to future ferroelectric memories," in *2013 IEEE International Electron Devices Meeting*, pp. 10–8, IEEE, 2013.

[56] S. Starschich, D. Griesche, T. Schneller, and U. Böttger, "Chemical solution deposition of ferroelectric hafnium oxide for future lead free ferroelectric devices," *ECS Journal of Solid State Science and Technology* **4**(12), pp. P419–P423, 2015.

[57] L. Xu, T. Nishimura, S. Shibayama, T. Yajima, S. Migita, and A. Toriumi, "Kinetic pathway of the ferroelectric phase formation in doped hfo2 films," *Journal of Applied Physics* **122**(12), p. 124104, 2017.

[58] T. Shimizu, K. Katayama, T. Kiguchi, A. Akama, T. J. Konno, O. Sakata, and H. Funakubo, "The demonstration of significant ferroelectricity in epitaxial y-doped hfo2 film," *Scientific Reports* **6**, p. 32931, 2016.

[59] S. J. Kim, D. Narayan, J.-G. Lee, J. Mohan, J. S. Lee, J. Lee, H. S. Kim, Y.-C. Byun, A. T. Lucero, C. D. Young, *et al.*, "Large ferroelectric polarization of tin/hf0.5zr0.5o2/tin capacitors due to stress-induced crystallization at low thermal budget," *Applied Physics Letters* **111**(24), p. 242901, 2017.

[60] M. Hyuk Park, H. Joon Kim, Y. Jin Kim, W. Lee, H. Kyeom Kim, and C. Seong Hwang, "Effect of forming gas annealing on the ferroelectric properties of hf0.5zr0.5o2 thin films with and without pt electrodes," *Applied Physics Letters* **102**(11), p. 112914, 2013.

[61] M. H. Park, H. J. Kim, Y. J. Kim, W. Lee, T. Moon, K. D. Kim, and C. S. Hwang, "Study on the degradation mechanism of the ferroelectric properties of thin hf0.5zr0.5o2 films on tin and ir electrodes," *Applied Physics Letters* **105**(7), p. 072902, 2014.

[62] M. Hoffmann, U. Schroeder, T. Schenk, T. Shimizu, H. Funakubo, O. Sakata, D. Pohl, M. Drescher, C. Adelmann, R. Materlik, *et al.*, "Stabilizing the ferroelectric phase in doped hafnium oxide," *Journal of Applied Physics* **118**(7), p. 072006, 2015.

[63] K. Florent, S. Lavizzari, M. Popovici, L. Di Piazza, U. Celano, G. Groeseneken, and J. Van Houdt, "Understanding ferroelectric al: Hfo2 thin films with si-based electrodes for 3d applications," *Journal of Applied Physics* **121**(20), p. 204103, 2017.

[64] T. Böscke, J. Müller, D. Bräuhaus, U. Schröder, and U. Böttger, "Ferroelectricity in hafnium oxide thin films," *Applied Physics Letters* **99**(10), p. 102903, 2011.

[65] S. Starschich, T. Schenk, U. Schroeder, and U. Boettger, "Ferroelectric and piezoelectric properties of hf1-xzrxo2 and pure zro2 films," *Applied Physics Letters* **110**(18), p. 182905, 2017.

[66] T. Shimizu, T. Yokouchi, T. Shiraishi, T. Oikawa, P. S. R. Krishnan, and H. Funakubo, "Study on the effect of heat treatment conditions on metalorganic-chemical-vapor-deposited ferroelectric hf0.5zr0.5o2 thin film on ir electrode," *Japanese Journal of Applied Physics* **53**(9S), p. 09PA04, 2014.

[67] M. Hyuk Park, H. Joon Kim, Y. Jin Kim, T. Moon, and C. Seong Hwang, "The effects of crystallographic orientation and strain of thin hf0.5zr0.5o2 film on its ferroelectricity," *Applied Physics Letters* **104**(7), p. 072901, 2014.

[68] T. Shiraishi, K. Katayama, T. Yokouchi, T. Shimizu, T. Oikawa, O. Sakata, H. Uchida, Y. Imai, T. Kiguchi, T. J. Konno, *et al.*, "Impact of mechanical stress on ferroelectricity in (hf0.5zr0.5)o2 thin films," *Applied Physics Letters* **108**(26), p. 262904, 2016.

[69] R. Materlik, C. Künneth, and A. Kersch, "The origin of ferroelectricity in hf1-xzrxo2: A computational investigation and a surface energy model," *Journal of Applied Physics* **117**(13), p. 134109, 2015.

[70] M. H. Park, Y. H. Lee, H. J. Kim, T. Schenk, W. Lee, K. Do Kim, F. P. Fengler, T. Mikolajick, U. Schroeder, and C. S. Hwang, "Surface and grain boundary energy as the key enabler of ferroelectricity in nanoscale hafnia-zirconia: a comparison of model and experiment," *Nanoscale* **9**(28), pp. 9973–9986, 2017.

[71] J. Muller, T. S. Böscke, U. Schröder, S. Mueller, D. Bräuhaus, U. Böttger, L. Frey, and T. Mikolajick, "Ferroelectricity in simple binary zro_2 and hfo_2," *Nano Letters* **12**(8), pp. 4318–4323, 2012.

[72] T. D. Huan, V. Sharma, G. A. Rossetti Jr, and R. Ramprasad, "Pathways towards ferroelectricity in hafnia," *Physical Review B* **90**(6), p. 064111, 2014.

[73] J. Müller, T. Böscke, D. Bräuhaus, U. Schröder, U. Böttger, J. Sundqvist, P. Kücher, T. Mikolajick, and L. Frey, "Ferroelectric zr0.5hf0.5o2 thin films for nonvolatile memory applications," *Applied Physics Letters* **99**(11), p. 112901, 2011.

[74] M. Hyuk Park, H. Joon Kim, Y. Jin Kim, W. Lee, T. Moon, and C. Seong Hwang, "Evolution of phases and ferroelectric properties of thin hf0.5zr0.5o2 films according to the thickness and annealing temperature," *Applied Physics Letters* **102**(24), p. 242905, 2013.

[75] S. Riedel, P. Polakowski, and J. Müller, "A thermally robust and thickness independent ferroelectric phase in laminated hafnium zirconium oxide," *AIP Advances* **6**(9), p. 095123, 2016.

[76] A. N. Morozovska, M. D. Glinchuk, and E. A. Eliseev, "Phase transitions induced by confinement of ferroic nanoparticles," *Physical Review B* **76**(1), p. 014102, 2007.

[77] M. J. Polking, J. J. Urban, D. J. Milliron, H. Zheng, E. Chan, M. A. Caldwell, S. Raoux, C. F. Kisielowski, J. W. Ager III, R. Ramesh, *et al.*, "Size-dependent polar ordering in colloidal gete nanocrystals," *Nano Letters* **11**(3), pp. 1147–1152, 2011.

[78] C.-H. Lu, J. M. Raitano, S. Khalid, L. Zhang, and S.-W. Chan, "Cubic phase stabilization in nanoparticles of hafnia-zirconia oxides: Particle-size and annealing environment effects," *Journal of Applied Physics* **103**(12), p. 124303, 2008.

[79] P. Shen and W. Lee, "(111)-specific coalescence twinning and martensitic transformation of tetragonal zro2 condensates," *Nano Letters* **1**(12), pp. 707–711, 2001.

[80] D. Vollath, F. Fischer, M. Hagelstein, and D. Szabó, "Phases and phase transformations in nanocrystalline zro2," *Journal of Nanoparticle Research* **8**(6), pp. 1003–1016, 2006.

[81] Y. Wei, P. Nukala, M. Salverda, S. Matzen, H. J. Zhao, J. Momand, A. S. Everhardt, G. Agnus, G. R. Blake, P. Lecoeur, *et al.*, "A rhombohedral ferroelectric phase in epitaxially strained hf0.5zr0.5o2 thin films," *Nature Materials* **17**(12), p. 1095, 2018.

[82] M. H. Park, Y. H. Lee, T. Mikolajick, U. Schroeder, and C. S. Hwang, "Review and perspective on ferroelectric hfo2-based thin films for memory applications," *MRS Communications* **8**(3), pp. 795–808, 2018.

[83] J. Müller, P. Polakowski, S. Mueller, and T. Mikolajick, "Ferroelectric hafnium oxide based materials and devices: Assessment of current status and future prospects," *ECS Journal of Solid State Science and Technology* **4**(5), pp. N30–N35, 2015.

[84] T. Mikolajick, S. Slesazeck, M. H. Park, and U. Schroeder, "Ferroelectric hafnium oxide for ferroelectric random-access memories and ferroelectric field-effect transistors," *MRS Bulletin* **43**(5), pp. 340–346, 2018.

[85] J. Müller, E. Yurchuk, T. Schlösser, J. Paul, R. Hoffmann, S. Müller, D. Martin, S. Slesazeck, P. Polakowski, J. Sundqvist, *et al.*, "Ferroelectricity in hfo2 enables nonvolatile data storage in 28 nm hkmg," in *2012 Symposium on VLSI Technology (VLSIT)*, pp. 25–26, IEEE, 2012.

[86] P. Zubko and J.-M. Triscone, "Applied physics: A leak of information," *Nature* **460**(7251), p. 45, 2009.

[87] C. Ge, C. Wang, K.-j. Jin, H.-b. Lu, and G.-z. Yang, "Recent progress in ferroelectric diodes: explorations in switchable diode effect," *Nano-Micro Letters* **5**(2), pp. 81–87, 2013.

[88] E. Y. Tsymbal and H. Kohlstedt, "Tunneling across a ferroelectric," *Science* **313**(5784), pp. 181–183, 2006.

[89] M. Y. Zhuravlev, R. F. Sabirianov, S. Jaswal, and E. Y. Tsymbal, "Giant electroresistance in ferroelectric tunnel junctions," *Physical Review Letters* **94**(24), p. 246802, 2005.

[90] V. Garcia, S. Fusil, K. Bouzehouane, S. Enouz-Vedrenne, N. D. Mathur, A. Barthelemy, and M. Bibes, "Giant tunnel electroresistance for non-destructive readout of ferroelectric states," *Nature* **460**(7251), p. 81, 2009.

[91] P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf, and S. V. Kalinin, "Polarization control of electron tunneling into ferroelectric surfaces," *Science* **324**(5933), pp. 1421–1425, 2009.

[92] P. Blom, R. Wolf, J. Cillessen, and M. Krijn, "Ferroelectric schottky diode," *Physical Review Letters* **73**(15), p. 2107, 1994.

[93] F. Ambriz-Vargas, G. Kolhatkar, R. Thomas, R. Nouar, A. Sarkissian, C. Gomez-Yáñez, M. Gauthier, and A. Ruediger, "Tunneling electroresistance effect in a pt/hf0.5zr0.5o2/pt structure," *Applied Physics Letters* **110**(9), p. 093106, 2017.

[94] S. Fujii, Y. Kamimuta, T. Ino, Y. Nakasaki, R. Takaishi, and M. Saitoh, "First demonstration and performance improvement of ferroelectric hfo2-based resistive switch with low operation current and intrinsic diode property," in *2016 IEEE Symposium on VLSI Technology*, pp. 1–2, IEEE, 2016.

[95] L. Chen, T.-Y. Wang, Y.-W. Dai, M.-Y. Cha, H. Zhu, Q.-Q. Sun, S.-J. Ding, P. Zhou, L. Chua, and D. W. Zhang, "Ultra-low power hf0.5zr0.5o2 based ferroelectric tunnel junction synapses for hardware neural network applications," *Nanoscale* **10**(33), pp. 15826–15833, 2018.

[96] F. Ambriz-Vargas, G. Kolhatkar, M. Broyer, A. Hadj-Youssef, R. Nouar, A. Sarkissian, R. Thomas, C. Gomez-Yáñez, M. A. Gauthier, and A. Ruediger, "A complementary metal oxide semiconductor process-compatible ferroelectric tunnel junction," *ACS Applied Materials & Interfaces* **9**(15), pp. 13262–13268, 2017.

[97] A. Chouprik, A. Chernikova, A. Markeev, V. Mikheev, D. Negrov, M. Spiridonov, S. Zarubin, and A. Zenkevich, "Electron transport across ultrathin ferroelectric hf0.5zr0.5o2 films on si," *Microelectronic Engineering* **178**, pp. 250–253, 2017.

[98] E. Y. Tsymbal, A. Gruverman, V. Garcia, M. Bibes, and A. Barthélémy, "Ferroelectric and multiferroic tunnel junctions," *MRS Bulletin* **37**(2), pp. 138–143, 2012.

[99] M. Julliere, "Tunneling between ferromagnetic films," *Physics Letters A* **54**(3), pp. 225–226, 1975.

[100] K. Tsunekawa, D. D. Djayaprawira, M. Nagai, H. Maehara, S. Yamagata, N. Watanabe, S. Yuasa, Y. Suzuki, and K. Ando, "Giant tunneling magnetoresistance effect in low-resistance cofeb/ mgo (001)/ cofeb magnetic tunnel junctions for read-head applications," *Applied Physics Letters* **87**(7), p. 072503, 2005.

[101] W. J. Gallagher and S. S. Parkin, "Development of the magnetic tunnel junction mram at ibm: From first junctions to a 16-mb mram demonstrator chip," *IBM Journal of Research and Development* **50**(1), pp. 5–23, 2006.

[102] Y. Wei, S. Matzen, T. Maroutian, G. Agnus, M. Salverda, P. Nukala, Q. Chen, J. Ye, P. Lecoeur, and B. Noheda, "Magnetic tunnel junctions based on ferroelectric hf0.5zr0.5o2 tunnel barriers," *Physical Review Applied* **12**(3), p. 031001, 2019.

[103] C. Ederer and N. A. Spaldin, "Weak ferromagnetism and magnetoelectric coupling in bismuth ferrite," *Physical Review B* **71**(6), p. 060401, 2005.

[104] T. Kimura, "Spiral magnets as magnetoelectrics," *Annu. Rev. Mater. Res.* **37**, pp. 387–413, 2007.

[105] R. Ramesh and N. A. Spaldin, "Multiferroics: progress and prospects in thin films," *Nature Materials* **6**(1), p. 21, 2007.

[106] W. Eerenstein, N. Mathur, and J. F. Scott, "Multiferroic and magnetoelectric materials," *Nature* **442**(7104), p. 759, 2006.

[107] V. Garcia, M. Bibes, L. Bocher, S. Valencia, F. Kronast, A. Crassous, X. Moya, S. Enouz-Vedrenne, A. Gloter, D. Imhoff, *et al.*, "Ferroelectric control of spin polarization," *Science* **327**(5969), pp. 1106–1110, 2010.

[108] M. Fiebig, "Revival of the magnetoelectric effect," *Journal of Physics D: Applied Physics* **38**(8), p. R123, 2005.

[109] M. Bibes and A. Barthelemy, "Oxide spintronics," *IEEE Transactions on Electron Devices* **54**(5), pp. 1003–1023, 2007.

[110] S. Salahuddin and S. Datta, "Use of negative capacitance to provide voltage amplification for low power nanoscale devices," *Nano Letters* **8**(2), pp. 405–410, 2008.

[111] T. N. Theis and P. M. Solomon, "It's time to reinvent the transistor!," *Science* **327**(5973), pp. 1600–1601, 2010.

[112] V. V. Zhirnov and R. K. Cavin, "Nanoelectronics: Negative capacitance to the rescue?," *Nature Nanotechnology* **3**(2), p. 77, 2008.

[113] T. N. Theis and P. M. Solomon, "In quest of the "next switch": prospects for greatly reduced power dissipation in a successor to the silicon field-effect transistor," *Proceedings of the IEEE* **98**(12), pp. 2005–2014, 2010.

[114] A. M. Ionescu and H. Riel, "Tunnel field-effect transistors as energy-efficient electronic switches," *Nature* **479**(7373), p. 329, 2011.

[115] A. I. Khan, K. Chatterjee, B. Wang, S. Drapcho, L. You, C. Serrao, S. R. Bakaul, R. Ramesh, and S. Salahuddin, "Negative capacitance in a ferroelectric capacitor," *Nature Materials* **14**(2), p. 182, 2015.

[116] M. Hoffmann, F. P. Fengler, M. Herzig, T. Mittmann, B. Max, U. Schroeder, R. Negrea, P. Lucian, S. Slesazeck, and T. Mikolajick, "Unveiling the double-well energy landscape in a ferroelectric layer," *Nature* **565**(7740), p. 464, 2019.

[117] J. Iniguez, P. Zubko, I. Lukyanchuk, and A. Cano, "Ferroelectric negative capacitance," *Nature Reviews Materials* **4**, p. 1, 2019.

[118] M. Hoffmann, M. Pešić, K. Chatterjee, A. I. Khan, S. Salahuddin, S. Slesazeck, U. Schroeder, and T. Mikolajick, "Direct observation of negative capacitance in polycrystalline ferroelectric hfo2," *Advanced Functional Materials* **26**(47), pp. 8643–8649, 2016.

[119] M. Kobayashi and T. Hiramoto, "On device design for steep-slope negative-capacitance field-effect-transistor operating at sub-0.2 v supply voltage with ferroelectric hfo2 thin film," *AIP Advances* **6**(2), p. 025113, 2016.

[120] M. Kobayashi, N. Ueyama, K. Jang, and T. Hiramoto, "Experimental study on polarization-limited operation speed of negative capacitance fet with ferroelectric hfo2," in *2016 IEEE International Electron Devices Meeting (IEDM)*, pp. 12–3, IEEE, 2016.

[121] https://www.rug.nl/about-us/news-and-events/news/archief2013/nieuwsberichten/feeling-the-pressure.

[122] M. H. Park, H. J. Kim, Y. J. Kim, T. Moon, K. Do Kim, and C. S. Hwang, "Toward a multifunctional monolithic device based on pyroelectricity and the electrocaloric effect of thin antiferroelectric hfxzr1-xo2 films," *Nano Energy* **12**, pp. 131–140, 2015.

[123] M. Hoffmann, U. Schroeder, C. Künneth, A. Kersch, S. Starschich, U. Böttger, and T. Mikolajick, "Ferroelectric phase transitions in nanoscale hfo2 films enable giant pyroelectric energy conversion and highly efficient supercapacitors," *Nano Energy* **18**, pp. 154–164, 2015.

[124] M. H. Park, T. Schenk, M. Hoffmann, S. Knebel, J. Gärtner, T. Mikolajick, and U. Schroeder, "Effect of acceptor doping on phase transitions of hfo2 thin films for energy-related applications," *Nano Energy* **36**, pp. 381–389, 2017.

[125] S. J. Russell and P. Norvig, *Artificial intelligence: a modern approach*, Malaysia; Pearson Education Limited,, 2016.

[126] D. Kuzum, S. Yu, and H. P. Wong, "Synaptic electronics: materials, devices and applications," *Nanotechnology* **24**(38), p. 382001, 2013.

[127] S. Boyn, J. Grollier, G. Lecerf, B. Xu, N. Locatelli, S. Fusil, S. Girod, C. Carrétéro, K. Garcia, S. Xavier, *et al.*, "Learning through ferroelectric domain dynamics in solid-state synapses," *Nature Communications* **8**, p. 14736, 2017.

[128] H. Mulaosmanovic, J. Ocker, S. Müller, M. Noack, J. Müller, P. Polakowski, T. Mikolajick, and S. Slesazeck, "Novel ferroelectric fet based synapse for neuromorphic systems," in *2017 Symposium on VLSI Technology*, pp. T176–T177, IEEE, 2017.

[129] S. Oh, T. Kim, M. Kwak, J. Song, J. Woo, S. Jeon, I. K. Yoo, and H. Hwang, "Hfzrox-based ferroelectric synapse device with 32 levels of conductance states for neuromorphic applications," *IEEE Electron Device Letters* **38**(6), pp. 732–735, 2017.